

# PATENT SPECIFICATION



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## COMPLETE SPECIFICATION

### Improvements relating to Aluminium Alcoholate Derivatives.

We, HARDMAN & HOLDEN LIMITED, a British Company, of Canal Street, Manchester, 10, and JACOBUS RINSE, a Dutch Subject, of Bernardsville, New Jersey, 5 United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the 10 following statement:—

This invention relates to new aluminium alcoholate derivatives and processes by which they may be produced.

An object of the present invention is to 15 produce a series of aluminium alcoholates having properties rendering them suitable for use in the coating industries in paints, varnishes, lacquers, linoleum, inks and in other fields where polymerizable compounds 20 and resins are of utility, and as cross-linking agents, driers and gelling agents in the production of resinous masses and rubbers for use in the above and other fields.

The novel compounds of the present invention are simple reaction products or 25 polymerization products produced therefrom, derived by heating an aluminium alcoholate of a normal or iso-monohydroxy alcohol containing from 3 to 10 carbon atoms with a monoalkylene glycol having 30 at least 6 carbon atoms, or a poly-alkylene glycol having 3 or 4 carbon atoms in the alkylene radical, the number of alkylene radicals being from 2 to 10, the 35 glycol having more carbon atoms than the alcohol from which the alcoholate is derived.

Suitable glycols having at least six carbon atoms include hexylene glycol and 40 octylene glycol.

Other suitable glycols are di- or other polypropylene glycol, or di or other polybutylene glycol. Other glycols tested, such as single glycols of 2 to 4 carbon atoms 45 and other polyalkylene glycols such as poly-

ethylene glycols are unsatisfactory for the purposes herein described.

The aluminium alcoholates to be reacted with the polyalkylene glycols mentioned above are preferably lower molecular weight 50 alcoholates such as aluminium alcoholates of isopropyl, butyl and isobutyl alcohols. Aluminium alcoholates of other normal—and iso-monohydroxy alcohols having from 3 to 10 carbon atoms can be employed. 55

Another special class of new aluminium alcoholate derivatives contemplated by the present invention comprises aluminium compounds derived from the reaction of the polyalkylene glycols hereinbefore described with mixed alcoholates of aluminium wherein either 1 or 2 of the alcoholate groups of the aluminium alcoholates disclosed hereinbefore as the initial reactant is or are replaced by a radical of a compound 60 exhibiting keto-enol tautomerism (or two of them), the radical preferably being that of an emolic keto ester such as ethyl acetoacetate and ethyl laevulinate. Other esters of related structure and in particular those containing up to 9 carbon atoms, can be used. In place of the keto-esters there may be used the keto alcohols and diketones as acetonylacetone, pentanedione and diacetone alcohol. 75

This special class of aluminium alcoholate derivatives used as reactants herein may be obtained simply by heating an aluminium alcoholate of an aliphatic alcohol containing up to 4 carbon atoms with the keto ester, 80 keto alcohol or diketone in a quantity which replaces one or two of the lower alkyl radicals in the alcoholate. For example to 1 mol. of aluminium isopropoxide in the liquid state in a flask fitted for distillation was 85 added 1 mol. of ethyl acetoacetate through a tap funnel. The mixture was then heated until 1 mol. of isopropanol was distilled off. The product resulting from equi-molecular quantities of alcoholate and keto ester is 90

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a liquid having reduced activity for hydroxyl groups. The product has only two alkoxy groups per atom and accordingly its reactivity is reduced from 3 to 2. In a number of cases the higher alcoholates derived from these intermediate alcoholates will react more smoothly or more slowly than the higher alcoholates derived from the simple alcoholates, hereinbefore described.

10 The reaction of the polyalkylene glycol with the aluminium alcoholate may be carried out simply by mixing these two materials and heating the mixture to a temperature at which they react, generally 70-

15 150°C. Reaction is greatly facilitated by heating the reaction mixture to a temperature which vaporises off the alcohol split off from the aluminium alcoholate. When the reaction is complete and the mass is cooled, 20 a viscous resinous mass or solid is obtained.

In preferred operations, the dipropylene glycol or other polyalkylene glycol containing 3 or 4 carbon atoms in the alkylene radical is mixed with the aluminium isopropylate or other aluminium alcoholate in the molar ratio of 1:2. When this proportion of dipropylene glycol and aluminium isopropylate is used, compounds are formed which appear to have the following typical

30 formula:—

$(RO)_2Al-O(CH_2)_nO(CH_2)_nO-Al(OR)_2$ ,  
wherein the R's are isopropyl radicals. The polyalkylene glycols and the aluminium alcoholates may, however, be mixed or reacted in other proportions, i.e. in the ratio of 0.5-2 of the former, to 2 of the latter and the resulting reaction masses may be employed for the purposes hereinbefore described. When a larger proportion of the 40 glycol is used, harder resins are obtained but their gelling properties are still comparable to those of the reaction products produced using the ratio of 1:2.

In accordance with a further embodiment 45 of the invention, the reaction products of the aluminium alcoholates and glycols discussed above are further reacted with a monohydroxy alcohol having more than 8 carbon atoms. Saturated and unsaturated 50 fatty alcohols, having from 12 to 18 or more carbon atoms are preferred. When the aluminium alcoholates, glycol and monohydroxy compound are reacted in bulk or stepwise in the molar ratio of 1:1:1, a new 55 series of soluble and meltable polymers are obtained. The ratio of the reactants, however, may be varied in accordance with known principles to provide ultimate products which are either more liquid or 60 harder.

During the reactions, the lower alcohol of the aluminium alcoholates is split off and may be removed by distillation. Some of the resulting products in this class may be 65 made up into coating compositions and

stored indefinitely without hardening, but will solidify and harden quickly when spread in the form of a thin layer by absorbing water vapour from the air. The particular mechanism by which the mixture 70 of aluminium alcoholate and the glycol, with or without the monohydroxy compound, polymerises or hardens has not been determined.

The compositions of the invention may 75 contain or be employed in conjunction with other materials such as solvents, oils, resins, pigments, colours, plasticisers and driers.

#### EXAMPLE 1.

80 204 gms. of aluminium isopropoxide were dissolved in 360 gms. of white spirit and 146 gms. of octylene glycol added with vigorous shaking. The mixture was then distilled under a partial vacuum. 120 gms. 85 of isopropanol together with some white spirit were removed. Upon cooling a clear colourless solution resulted.

The octylene glycol in the foregoing process may be replaced by other glycols having 90 longer hydrocarbon chains. Similar products may be obtained with properties differing in various respects.

#### EXAMPLE 2.

95 The dry resin product produced in a quantity of 230 grams by distilling off the white spirit from the resin solution obtained in Example 1 is heated with 284 grams of stearyl alcohol until 60 grams of isopropyl alcohol have been distilled off and a temperature of 250° is reached. The liquid product obtained becomes viscous on cooling and finally sets in the form of a soft wax which will dry to a hard wax when spread in a 105 thin layer.

#### EXAMPLE 3.

100 Aluminium butylate in a quantity of 246 gms. is melted and mixed with 59 grams 110 of hexylene glycol. The mass is then heated until 60 grams of butanol have been vaporised. A resinous product is obtained.

#### EXAMPLE 4.

115 The resin obtained by the process of Example 3 is mixed with 564 grams of oleyl alcohol. The resulting liquid dries to a soft wax when exposed to the atmosphere. 120

#### EXAMPLE 5.

125 134 grams of dipropylene glycol is added to 408 grams of aluminium isopropylate and the mixture is heated to 100 to 120°C. at which temperature isopropanol is separated by distillation. 120 grams of this alcohol are collected. The resulting product on cooling provides a viscous resinous or solid mass which is easily soluble in benzene. 130

In the above procedure, other polypylene glycols of 3 to 10 alkylene radicals may be substituted, and corresponding products are obtained.

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#### EXAMPLE 6.

Hexapropylene glycol in a quantity of 402 grams is added to 592 grams of aluminium isobutyrate and the mixture is heated to 120 to 140°C. until 148 grams of isobutanol are distilled off. The resulting product is soluble in mineral spirits in every ratio and possesses the properties herein defined.

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#### EXAMPLE 7.

Dibutylene glycol in a quantity of 162 grams is mixed with aluminium propylate and the mixture is heated to 120 to 140°C. until 120 grams of propanol are liberated and separated by distillation. A solid mass is obtained which is soluble in aliphatic hydrocarbon solvents, and possesses the properties herein defined.

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#### EXAMPLE 8.

Aluminium isopropylate in a quantity of 400 grams is mixed with 260 grams of ethylacetacetate and heated together, and 120 grams of isopropanol are removed by distillation. Then 134 grams of di-propylene glycol are mixed and heat applied, and again 120 grams of isopropanol are removed by distillation. The resulting product will act as a drier for alkyds, and does not set at 20°C.

The novel aluminium alcoholate derivatives containing oxygen atoms in the connecting chain are particularly effective for thickening or gelling alkyd resins and other hydroxyl-containing oils and resins. Very smooth masses are obtained, for grains or gel particles of varying hardness are not formed. For example, when 1% of the new aluminium alcoholate is added to a soya bean oil-modified glycerol alkyd resin of 30% phthalic anhydride content, a thickened product is obtained having excellent properties for use in coating compositions. Also, when 3% of an aluminium alcoholate derivative of the invention is added to linseed oil, coating compositions containing the same have improved drying characteristics.

The new aluminium alcoholate derivatives of the invention are particularly suitable as gelling agents when the number of alkylene radicals is from 3 to 10. The aluminium alcoholate derivatives of the invention constitute cross-linking agents for the production of rubbery products of great durability from polyesters of a molecular weight of from 10,000 to 100,000 derived from polypropylene glycol and dicarboxylic acids. Polyester rubbers have heretofore been produced from such

reactants using di-isocyanate as cross-linking agents as is disclosed in the Kirk-Othmer Encyclopedia of Chemical Technology, Volume II, page 845. By substitution of the aluminium alcoholate derivatives of the present invention for the di-isocyanates in the compositions described in said text, rubbery products of superior durability are obtained. In a typical procedure, ethylene glycol or propylene glycol is mixed with adipic acid or other dicarboxylic acid to produce lower molecular weight polyesters having a molecular weight of from 2000 to 3000. The addition of the aluminium alcoholate derivative to this mass yields high molecular polymers of rubber-like properties.

The aluminium alcoholate derivatives of the present invention find utility, also, when employed in admixture with fatty amide and polyamide resins. Such resins dry rapidly probably because  $\text{ROCNH}_2$  (where R is an alkyl radical) isomerizes to the enol form  $\text{RC(OH)=NH}$  which reacts by means of its hydroxyl group liberating the alcohol of the amide. These resins containing the aluminium alcoholate derivatives comprise viscous oils or resins which can be solidified or dried simply by exposure of the same to the humidity in the atmosphere. When applied in the form of a coating, the surfaces dry hard and tack-free.

The polyamide resins to which the aluminium alcoholate derivatives may be added in accordance with this utility are described in Kirk-Othmer, supra, Volume 10, page 933. They are made from dimer fatty acids and amines.

The aluminium alcoholate derivatives are added to the fatty polyamide resins in a molar ratio preferably of 1:2 but the ratio may vary from 1:10 to 1:1. The reaction may be brought about without heating but it is preferable to heat the mixture and remove the liberated alcohol by distillation.

The action of the aluminium alcoholate derivatives is particularly effective with polyamide resins made from dimerized fatty acids, ethylene diamine and diethylene triamine. Such products having acid values below 10 are sticky compounds which are suitable for use as heat-sealing resins and also may be employed in combination with epoxy resins. Upon reaction with aluminium alcoholate derivatives resins are formed which dry tack-free in a short time and remain tough and flexible.

In a specific example of the use of the alcoholate derivatives, 20 grams of a soft resinous condensation product of dimer linoleic acid with diethylene triamine, containing 5.7% nitrogen in the resin, are heated with 4 grams of the dipropylene glycol-aluminium isopropylate reaction product which has been dissolved in 20 grams of a 1:1 mixture of butanol and xylo. When

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grams of isopropanol have been distilled off, a resin solution is obtained which when applied as a coating dries rapidly by the absorption of moisture from the air to provide a hard, tack-free surface.

It should be understood that the present invention is not limited as to the specific details of procedures, compounds or compositions herein disclosed but that it extends to all equivalents which will occur to those skilled in the art upon consideration of the scope of the claims appended hereto.

**15 What we claim is:**

1. A process for producing aluminium alcoholate derivatives comprising heating an aluminium alcoholate of a normal or iso-monohydroxy alcohol containing from 3 to 20 carbon atoms with a monoalkylene glycol having at least 6 carbon atoms or a polyalkylene glycol having 2-10 radicals each containing 3 or 4 carbon atoms, the glycol having more carbon atoms than an alkoxy group of the alcoholate used as starting material.

2. A process as claimed in Claim 1, in which the aluminium alcoholate has one or two alkoxy groups replaced by one or 30 two radicals of a compound exhibiting keto-enol tautomerism, preferably of an enolic keto ester such as ethylacetacetate.

3. A process as claimed in Claim 1 or 2, in which the aluminium alcoholate and 35 the polyalkylene glycol are used in respective molar ratios of 2:0.5 to 2.

4. A process for producing aluminium alcoholate derivatives which comprises reacting a monohydroxy alcohol having more 40 than 8 carbon atoms with a condensation product obtained by the process according to Claim 1.

5. A process for producing improved resinous masses which comprises reacting 45 an alkyd resin containing at least one free hydroxy group with a condensation product obtained from the process described according to Claim 3.

6. A process for producing improved 50 resinous masses which comprises reacting a polyamide resin with a condensation product obtained by the process according to Claim 3.

7. A condensation product of an alu-

minium alcoholate of a normal or iso-mono-55 hydroxy alcohol containing from 3 to 10 carbon atoms with a poly-alkylene glycol having 2-10 alkylene radicals each containing 3 or 4 carbon atoms, said glycol having more carbon atoms than an alkoxy group 60 of the alcoholate used.

8. A condensation product of an aluminium alcoholate of a monohydroxy alcohol having 3-10 carbon atoms with a polyalkylene glycol having 2-10 alkylene radicals 65 each containing 3 or 4 carbon atoms condensed in respective molar ratios of 2:0.5 to 2, said glycol having more carbon atoms than an alkoxy group of the alcoholate used. 70

9. An improved resinous product, the reaction product of: (1) an alkyd resin containing at least one free hydroxy group with (2) the condensation product of (a) an aluminium alcoholate of a normal or iso-monohydroxy alcohol containing from 3 to 10 carbon atoms with (b) a polyalkylene glycol having 2-10 alkylene radicals each containing 3-4 carbon atoms condensed in respective molar ratios of from 4:1 to 1:1, said 80 glycol having more carbon atoms than the alkoxy group which it is desired to replace.

10. An improved resinous product, the reaction product of: (1) a polyamide resin with (2) the condensation product of (a) an 85 aluminium alcoholate of a normal or iso-monohydroxy alcohol containing from 3 to 10 carbon atoms with (b) a polyalkylene glycol having 2-10 alkylene radicals each containing 3 or 4 carbon atoms condensed 90 in respective molar ratios of 1:1 to 1:10 preferably 1:2, said glycol having more carbon atoms than the alkoxy group which it is desired to replace.

11. A process for producing aluminium 95 alcoholate derivatives, substantially as described.

12. Aluminium alcoholate derivatives prepared as described with reference to the foregoing examples 1-4. 100

13. A process for producing resinous masses, substantially as described.

14. Resinous products prepared from an aluminium alcoholate derivative as claimed in any of Claims 7, 8 and 12 and alkyd or 105 polyamide resins, substantially as described.

**MARKS & CLERK.**

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